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(54) **Method of painting elements made from plastics, and elements formed thereby**

(57) A method in which a surface of an element formed from a thermosetting synthetic plastics material which is to be painted, for example, a motor vehicle component formed from a composite such as SMC or BMC receives, before the normal layers of primer and paint, at least one layer of a polymerisable material, the said material, once polymerised, being able to form a layer that is impermeable to any gaseous substance and characterised by a temperature at which polymerisation occurs lower than the temperature of vaporisation of the monomers from which the said synthetic plastics material of the element to be painted is formed, for example, a catalysed two-component polyurethane transparent paint; following the application of the said layer of polymerisable material, the element is stoved at the polymerisation temperature of this material until it is completely polymerised and is then painted in a conventional way, applying the successive layers of paint to the said gas-impermeable polymerised layer and, finally, it is stoved at a high temperature (150°C) in order to polymerise the paint layers.

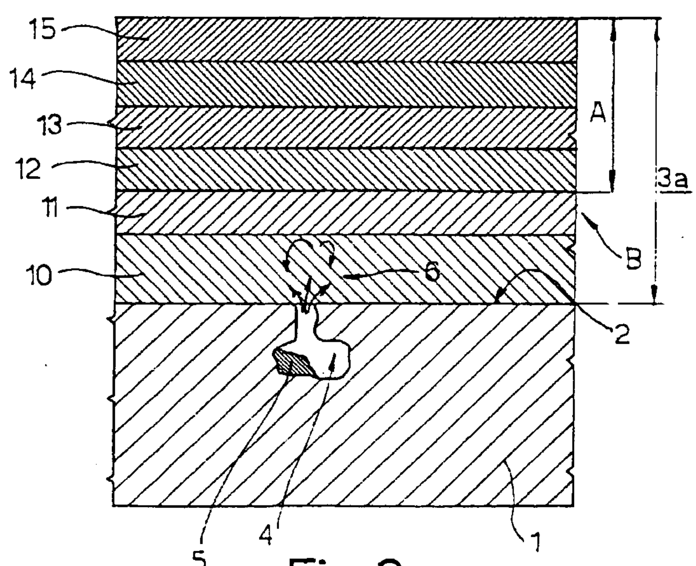

Fig. 2

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Description

The present invention concerns an improved method of painting applicable to elements formed from synthetic plastics materials, in particular, motor-vehicle body components made from composites, which avoids the risk of bubbles and/or blisters forming in the layer/layers of paint/paints. The invention also relates to elements formed from painted plastics material, which have a high quality of surface finish and do not require, except in exceptional cases, subsequent repairs to the paintwork.

It is known in the motor vehicle industry, that vehicle body components (bonnets, doors, etc) made from synthetic plastic materials are being used increasingly and these may be formed in complex shapes and/or with low weights, both of which factors are impossible to achieve with sheet steel elements of substantially the same dimensions. Composites such as SMC, BMC, etc based on thermosetting plastics resins of the vinyl ester/polyester type are preferably used to make such components.

Once moulded, such components must be painted with the same paints and, substantially, the same production cycle as sheet-steel parts in order to ensure perfect aesthetic conformity between parts of the same motor vehicle made from different materials. To this end, a base layer of an electroconductive material is applied directly to the surfaces of the plastics elements to be painted, this base usually comprising a single-component conductive primer which polymerises at a relatively high temperature (approximately 150°C).

Typically, the primer is spread in a layer of predetermined thickness (approximately 30 microns) and the treated element is then stoved in an oven, causing polymerisation of the primer layer which hardens to form a porous, transparent, conductive film on the surface of the plastics element to be painted. By virtue of the conductivity of the primer the element may then be painted by conventional methods as if it were an element made from sheet steel; this also improves the adhesion of the layers of paint applied successively to the surface of the element. After all the paint/paints have been applied, the elements are again stoved at a high temperature (150°C) to cause the polymerisation of the paint layers.

However, during the painting process described and, in particular, during the final stage of stoving of the painted elements, problems, such as the formation of bubbles or blisters in the paint layer, frequently arise; this occurs particularly frequently in the case of vehicle body parts formed from composites based on thermosetting resins such as BMC and SMC. This problem requires the elements upon which surface bubbles have developed to be repaired manually by means of sanding to remove the layer of paint ruined by the bubble, filling and repainting: this is slow and involves a significant increase in manufacturing costs; in addition, during the subsequent stoving of the repainted part, the problem of bubbles forming in the paint layer may arise again leading, in the most serious cases, to the component being discarded.

The problems described are the reason for the lack of extensive use, in the motor vehicle industry, of vehicle body parts made from composites, which use is instead limited to small-scale production, to cover so-called "niche" productions, such as special vehicles (convertibles, single-compartment family vehicles etc).

The aim of the invention is to provide an improved method of painting elements made from synthetic plastics materials, in particular vehicle body parts made from composites, which does not have the disadvantages described, in particular being free from the risk of bubbles forming in the paint layer during the stoving stage.

On this basis, the invention therefore provides a method of painting applicable to elements made from synthetic plastics material, in particular motor vehicle parts made from composites, including the steps of:

- firstly, applying at least one base layer of a predetermined thickness of a polymerisable electroconductive material to a surface of a said element to be painted and, subsequently applying at least one layer of paint on top of the said base layer of polymerisable material; and
- heating the element to a first predetermined temperature to cause the polymerisation of the said base layer of polymerisable electroconductive material;

characterised in that, before the said base layer of polymerisable electroconductive material is applied, the method includes the following steps:

(a) - applying a continuous layer of a second polymerisable material to the said surface to be painted, the said second material being of a type which, once polymerised, can form a layer which is impervious to any gaseous substance and which is completely polymerisable by heating to a second predetermined temperature below both the said first predetermined temperature and the lowest temperature of vaporisation of the monomers forming the said synthetic plastics material constituting the said element to be painted;

(b) - heating the element, with the said surface to be painted covered with the said layer of the second polymerisable material, to the said second predetermined temperature until the said second polymerisable material is completely polymerised;

in such a way that the layer of the said polymerisable electroconductive material is deposited, not directly on the said surface to be painted, but on a gas-impermeable layer formed from the said polymerised second material which covers the said surface to be painted completely.

In particular, the said element to be painted is formed from a material based on thermosetting vinyl ester/polyester resins, and the said second polymerisable material is constituted by a catalysed two-component polyurethane transparent paint which is completely polymerisable by heating to just 60°C. The said second polymerisable material is applied to a layer formed by a polyester-based adhesion promoter which is applied directly to the surface to be painted.

The invention also relates to a painted element formed from synthetic plastics material, in particular a vehicle-body component formed from a composite, comprising a panel pressed from at least one synthetic plastics resin, at least one visible surface of which is covered by a plurality of layers of polymerisable materials including at least one layer of paint; characterised in that the said plurality of layers of polymerisable materials comprise, in order, starting with the layer adjacent the said surface, a first, gas-impermeable layer, and a second, gas-permeable layer, both formed from respective different polymerised materials; the material forming the second layer having a chemical composition such that it forms an electroconductive primer for receiving the said at least one layer of paint, and which polymerises on heating to a first predetermined temperature substantially equal to that needed to polymerise the layer of paint; the material forming the first layer having a chemical composition such that it polymerises completely on heating to a second predetermined temperature below both the said first predetermined temperature and the lowest temperature of vaporisation of the monomers forming the said synthetic plastics resin from which the said panel is formed.

In this way, any risk that bubbles will form in the paint layer as a result of the final stoving to which the painted elements must be subjected to polymerise the layer/layers of paint applied is completely avoided. In fact, the Applicant has established by extensive experimentation that the formation of bubbles in the paint, a well known disadvantage which has until now greatly limited the extensive use of painted composite elements in a vehicle body, is due to the vaporisation, during stoving (which occurs at approximately 150°C), of a small proportion of the monomers, forming the resin/resins from which the element to be painted is formed which have not polymerised or are only partly polymerised and which, during the pressing, remain trapped in micropores, invisible to the naked eye, close to the surface of the element and in communication with the exterior.

However, the application of the catalysed two-component polyurethane paint layer directly to the surface to be painted (with the interposition solely of the adhesion promoter) and its polymerisation before the application of the conventional layers of primer and paint to the surface to be painted allows a gas-impermeable layer to be formed on the surface itself, forming a gas-tight seal over the surface pores which may contain unpolymerised or partially-polymerised monomers.

Consequently, when these vaporise during the final stoving of the painted element, the gases produced are no longer able to reach the painted surface and pass through the porous primer layer to penetrate the layers of paint being polymerised and so form the known bubbles. The polymerisation of the layer of gas-impermeable material at a low temperature (about 60°C), by virtue of the use of catalysed paints, also guarantees that no monomers can vaporise during the polymerisation of this sealing layer, risking localised damage in the layer which is still being polymerised, which could mean that the layer itself is not completely impermeable.

These and other characteristics of the invention will become clearer from the following description of a preferred embodiment, given by way of non-limitative example, with reference to the accompanying drawings, in which:

- Figure 1 represents schematically the mechanism by which bubbles are formed in a layer of paint applied to a surface of an element made from plastics material; and
- Figure 2 represents schematically in section the structure of a plastics element painted according to the invention.

With reference to Figures 1 and 2, the reference numeral 1 indicates an element formed from a synthetic plastics material, for example, a panel pressed from a composite material and forming a vehicle body part, for example, of a motor vehicle, such as a bonnet, a door, etc. Here and in the following description, the composites are considered, for simplicity, as a subclass of synthetic materials being, as is known, constituted by a reinforcing agent (glass, carbon, kevlar fibres, etc, regardless of how it is formed and distributed), encapsulated in a matrix constituted by one or more synthetic plastics resins obtained by the polymerisation of one or more monomers.

The panel or element 1 has a surface 2 covered by a paint coating 3 (possibly constituted by a plurality of superposed thinner layers of diverse materials); the surface 2 also contains pores 4 (only one of which is illustrated on an enlarged scale in Figure 1), at least some of which are partially filled with grains 5 of unpolymerised or only partially polymerised monomers; the grains 5 are formed from the same monomers as those used to form the resin/resins constituting the synthetic plastics base material from which (with the addition of the fillers) the element or panel 1 is made, and are the inevitable result of the known process for forming the panel or element 1 which is, for example, obtained by injection moulding, compression moulding, or injection-compression moulding.

In the present case described, which concerns elements 1 intended for motor vehicle bodies, the resin/resins forming the element or panel 1 are thermosetting vinyl ester/polyester resins as the element/panel 1 is

moulded from a composite of the SMC, BMC or similar type.

As determined by the Applicant, because of the microstructure of the panel/element 1, when the painted element 1 is heated to polymerise the multi-layered coating 3, the grain 5 vaporises creating gases (shown by the arrows 6) which, together with any air which may be trapped in the pore 4, expand and leave the pore 4, causing the coating 3 to swell which, as it is in the polymerising phase, is soft and plastic, although already mostly impermeable to gases; the gases 6 are thus not able to escape and they collect above the pore 4 and below the coating 3, creating a bubble 7. It has been determined that the sizes of the bubbles 7 are an order of magnitude greater than those in the pores 4, which may vary from several microns to several millimetres: consequently, the bubbles 7 which form are between 1 and 10 millimetres in diameter or more.

This fact confirms the validity of the interpretive model described above: if, in fact, the formation of the bubbles 7 were not due primarily to the vaporisation of monomers which are not 100% polymerised within the pores 4, the size of the bubbles would in practice be limited to 5/7 of those within the pores 4 (a value corresponding to the variation in volume of the air in the pores 4 caused by thermal expansion) and, consequently, only extremely small bubbles would form. In addition, the model is further confirmed by the fact that, in current practice, bubbles also form again at exactly the same places on elements 1 that have already experienced the phenomenon and which have been repaired (by sanding, filling and repainting of the places where bubbles formed), as soon as the piece is heated again to polymerise the paint in the repaired areas.

With reference to Figure 2, the known phenomenon illustrated in Figure 1 is avoided, according to the invention, by means of a particular structuring of the multi-layered coating 3. In practice, a coating 3a is formed according to the invention on the surface 2 and, starting with the layer adjacent the surface 2, comprises two superimposed films B and A; the film A corresponds to conventional coatings, such as that in Figure 1, while the film B includes, in turn, a first continuous layer 10 applied directly to the surface 2 to cover it completely, being approximately 30 microns thick and formed from a polyester-based adhesion promoter ("Barrier"), for example, 487567 from the firm PPG Industries Inc, USA, and a second layer 11, also continuous and applied directly to the layer 10 so as to cover the surface 2 completely, being between 30 and 40 microns thick and formed from a material which polymerises at low temperature (approximately 60°C) and is impermeable to gaseous substances such that the layer 10 is completely gas-impermeable.

In the present case, the layer 11 is formed from a catalysed two-component transparent polyurethane paint, such as, for example, 228003 obtained from PPG Industries Inc. The film A, instead, is, as already stated, constituted by a conventional multi-layer coating including, in the present case: a first layer 12 of thickness which may vary between 20 and 30 microns formed from an electrically-conductive polymerisable primer of the single-component type, for example, 487538, also from PPG Industries Inc, having a stoving temperature (for polymerisation) of about 150°C; a second layer 13, approximately 40 microns thick, formed from an undercoat paint, for example, "base coat" 400085/1 from HERBERTS GmbH, WUPPERTAL (D); a third layer 14, approximately 30 microns thick, formed from enamel and defining the real paint layer; and a surface layer 15 of approximately 30 microns thick, formed from a protective transparent polymer, for example, a "lacquer" of any known type.

According to the invention, the layer 10 is first of all applied, for example, by spraying to the surface 2 of the untreated element or panel 1 to be painted and then the layer 11 of two-component paint, which is applied by a "wet on wet" technique, that is, while the underlying film of material just applied is still wet due to the, as yet, incomplete evaporation of the solvent used. The element 1, with only the layers 10 and 11 covering the surface 2 completely, is then stoved in an oven at a temperature which causes the rapid polymerisation of the material forming the layer 11; since one is dealing with a catalysed paint, the latter polymerises completely in approximately 45 minutes on heating of the element 1 to merely 60°C. At such a low temperature, which is certainly below the lowest temperature of vaporisation of any monomers in the pores 4, these latter are not able to generate any gas whereby the layer 11 polymerises completely, thereby becoming impermeable to any gaseous substance rapidly and without any damage.

Once the polymerisation of the layer 11 is complete, the element 1 is cooled and the layer 12 of conductive primer is first applied thereto in a known way followed by the layers 13, 14, 15 of paint proper; these layers, starting from the base layer 12, are not however applied directly to the surface 2, as in the prior art, but to the layer 11 which, as already said, is completely impermeable to gases when fully polymerised; instead, the layer 12, which acts as a base for the in-line application of the three layers of paint 13, 14 and 15 by the same known methods as for body parts made from sheet steel is, as is known, porous and therefore permeable to gaseous substances which are able to diffuse through it, in the direction of the thickness, as already described in Figure 1.

Therefore, when the stoving stage necessary for polymerisation of the layer 12 is reached (as well as any subsequent stoving to cause the other layers of the film A to polymerise, whether separately or together), which step is executed by bringing the element 1 to a temperature of 140-160°C (on average 150°C) for approximately 30 minutes (always to a temperature much higher than that for the polymerisation of the layer 11), the gases which arise in the pores 4 (Figure 2) as a conse-

quence of the vaporisation of the monomers therein, leave the pores 4 to diffuse towards the film A but, before reaching the porous layer 12 which is still polymerising, encounter the gas-impermeable layer 11 which is already completely polymerised and therefore very rigid and of high mechanical strength. Consequently, the gases 6 are sealed in the pores 4, below the layer 11 and are therefore prevented from deforming the plastic layers 12-15 and creating bubbles 7. Any risk of the formation thereof is therefore avoided.

Claims

1. A method of painting applicable to elements formed from synthetic plastics materials, in particular components of motor vehicles formed from composites, including the steps of:

   - firstly applying at least one base layer of a predetermined thickness of a polymerisable electroconductive material to a surface of a said element to be painted and then applying at least one layer of paint on top of the said base layer of polymerisable material; and
   - heating the element to a first predetermined temperature to cause the polymerisation of the said base layer of polymerisable electroconductive material;

   characterised in that, before the said base layer of an polymerisable electroconductive material is applied, the method includes the following steps:

   (a) - applying a continuous layer of a second polymerisable material to the said surface to be painted, the said second material being of a type which, once polymerised, can form a layer which is impervious to any gaseous substance and which is completely polymerisable by heating to a second predetermined temperature below both the said first predetermined temperature and the lowest temperature of vaporisation of the monomers forming the said synthetic plastics material constituting the said element to be painted;
   (b) - heating the element, with the said surface to be painted covered with the said layer of second polymerisable material, to the said second predetermined temperature until the said second polymerisable material is completely polymerised;

   in such a way that the layer of the said polymerisable electroconductive material is deposited, not directly on the said surface to be painted, but onto a gas-impermeable layer formed from the said polymerised second material which covers the said surface to be painted completely.

2. A method according to Claim 1 in which the said element to be painted is formed from a material based on thermosetting vinyl ester/polyester resins, characterised in that the said second polymerisable material is constituted by a catalysed two-component polyurethane transparent paint.

3. A method according to Claim 2, characterised in that the said second polymerisable material is applied on top of the said surface to be painted to form thereon a layer of between 30 and 40 microns thick.

4. A method according to Claim 2 or Claim 3, characterised in that a layer of adhesion promoter for the said second polymerisable material is applied in direct contact with the said surface to be painted; this second polymerisable material being applied immediately on top of the said layer formed from the adhesion promoter.

5. A method according to Claim 4, characterised in that a polyester-based adhesion promoter ("Barrier") is used, applied to the said surface to be painted in a continuous layer at least 30 microns thick; and in that the said catalysed two-component polyurethane paint is chosen such that it is completely polymerised at a temperature of 60°C.

6. A method according to Claim 5, characterised in that the said second two-component polyurethane paint is delivered to the said surface by a "wet on wet" technique.

7. A method according to any one of Claims 2 to 6, characterised in that the said electroconductive polymerisable material is a single-component primer which is polymerisable by heating to a temperature of at least 140-150°C.

8. A painted element formed from a synthetic plastics material, in particular a vehicle body part formed from a composite material, comprising a panel pressed from at least one synthetic plastics resin, at least one visible surface of which is covered by a plurality of layers of polymerisable materials including at least one layer of paint; characterised in that the said plurality of layers of polymerisable materials comprise, in order, starting with the layer adjacent the said surface, a first, gas-impermeable layer, and a second, gas-permeable layer, both formed from respective different polymerised materials; the material forming the second layer having a chemical composition such that it forms an electroconductive primer for receiving the said at least one layer of paint, and which polymerises on heating to a first predetermined temperature, substan-

tially equal to that needed to polymerise the layer of paint; the material forming the first layer having a chemical composition such that it polymerises completely on heating to a second predetermined temperature below both the said first predetermined temperature and the lowest temperature of vaporisation of the monomers forming the said synthetic plastics resin from which the said panel is formed.

9. A painted element according to Claim 8, characterised in that the said panel is formed from at least one thermosetting vinyl ester/polyester-based resin; and in that the first layer is formed from a two-component polyurethane paint; the said first layer being between 30 and 40 microns thick and being applied over a layer of a material formed from a polyester-based adhesion promoter which is at least 30 microns thick applied directly to the said surface provided with the layer of paint.

PRIOR ART

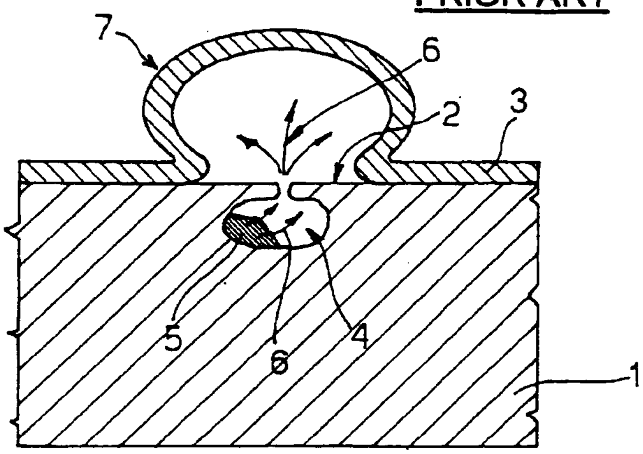

Fig. 1

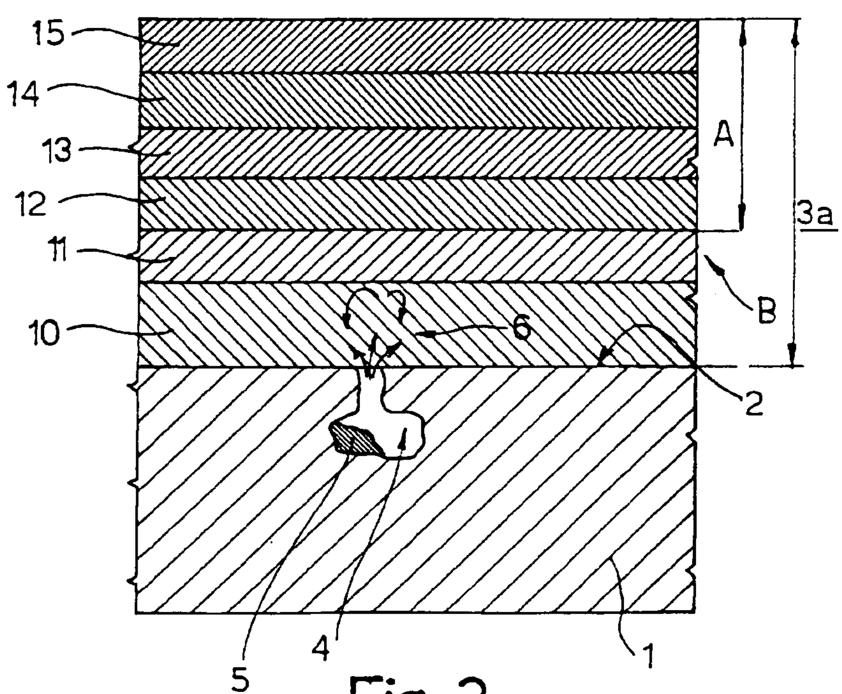

Fig. 2

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 96 11 0839

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	US-I-T982004 (L. KLUSENDORF ET AL.) 1 May 1979 * the whole document *	1,8	B05D1/00 B05D7/02 B05D1/04 B05D7/00
A	FR-A-2 695 048 (MANDUCHER ETS) 4 March 1994 * the whole document *	1,8	
P,A	EP-A-0 693 323 (BEE CHEMICAL CO) 24 January 1996 * the whole document *	1,8	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

B05D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	29 October 1996	Brothier, J-A

CATEGORY OF CITED DOCUMENTS

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